



Kinetic modeling of antimony(III) oxidation and sorption in soils



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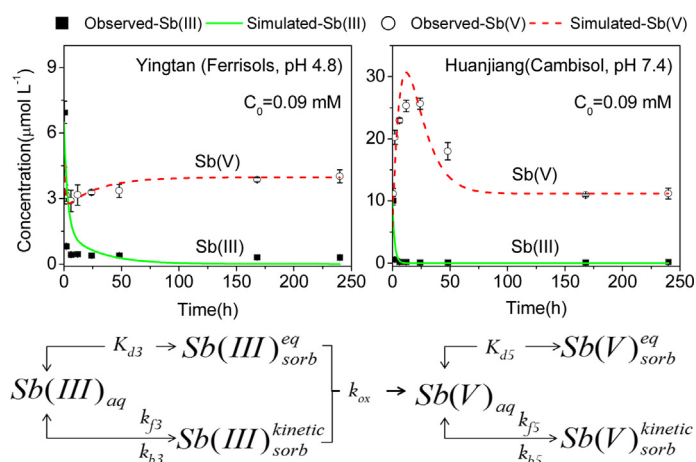
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HIGHLIGHTS

- Extensive retention and oxidation of Sb(III) in two soils with contrasting properties.
- Soil serve as a catalyst in promoting oxidation of Sb(III) even under anaerobic conditions.
- Transport of Sb(III) is governed by sorption-oxidation process on soil surfaces.
- The equilibrium-kinetic sorption and kinetic oxidation formulations successfully described Sb(III) reactions on soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Kinetic batch and saturated column experiments were performed to study the oxidation, adsorption and transport of Sb(III) in two soils with contrasting properties. Kinetic and column experiment results clearly demonstrated the extensive oxidation of Sb(III) in soils, and this can in return influence the adsorption and transport of Sb. Both sorption capacity and kinetic oxidation rate were much higher in calcareous Huanjiang soil than in acid red Yingtan soil. The results indicate that soil serve as a catalyst in promoting oxidation of Sb(III) even under anaerobic conditions. A PHREEQC model with kinetic formulations was developed to simulate the oxidation, sorption and transport of Sb(III) in soils. The model successfully described Sb(III) oxidation and sorption data in kinetic batch experiment. It was less successful in simulating the reactive transport of Sb(III) in soil columns. Additional processes such as colloid facilitated transport need to be quantified and considered in the model.

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1. Introduction

Antimony (Sb) and its compounds are considered to be pollutants of priority interest by the United States Environmental Protection Agency [1] and the European Union [2] because of their toxicity and suspected carcinogenicity for humans [3–6]. In general,

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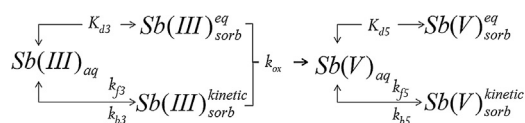


Fig. 1. A schematic diagram of the model. Here $Sb(III)_{aq}$ and $Sb(V)_{aq}$ are dissolved $Sb(III)$ and $Sb(V)$ in solution, $Sb(III)_{sorb}^{eq}$ and $Sb(V)_{sorb}^{eq}$ are $Sb(III)$ and $Sb(V)$ adsorbed on equilibrium sites, respectively, $Sb(III)_{sorb}^{kinetic}$ and $Sb(V)_{sorb}^{kinetic}$ are $Sb(III)$ and $Sb(V)$ adsorbed on kinetic sites, respectively, where K_{d3} , K_{d5} , k_{f3} , k_{b3} , k_{f5} , k_{b5} , and k_{ox} are the respective rates of reactions.

the natural abundance of Sb is low, $0.2\text{--}2\ \mu\text{g g}^{-1}$ in sediment rocks, $<1\ \mu\text{g L}^{-1}$ in natural water, and a few $\mu\text{g g}^{-1}$ in sediments and soils [2,7]. Because of Sb is frequently used in a variety of industrial products such as $Sb(III)$ in flame retardants and elemental Sb in alloys for storage batteries and ammunition [8,9], elevated concentrations of Sb are found in soil and water around mining and smelting sites, at shooting ranges, and along roadsides [10–13]. As the biggest Sb producer, China has suffered serious Sb pollution in several regions where soils were highly enriched in Sb [9] with concentration up to thousand times of natural background (a few $\mu\text{g g}^{-1}$) [2].

Although field and laboratory experiments have been carried out to investigate the environmental behaviors of Sb, there are still substantial knowledge gaps on the mobility of $Sb(III)$ in soils [2]. In the natural environment, $Sb(V)$ is the predominant species and exists as $Sb(OH)_6^-$ in oxic environments, and $Sb(III)$ primarily occurs as $Sb(OH)_3$ and is more stable and toxic under anaerobic conditions between pH 2 and 10 [2,7]. Understanding Sb speciation in soils and aquatic systems is important for assessing its fate and risk, because the mobility and toxicity of Sb greatly depend on its oxidation state. However, up to date most of the studies on Sb were only considered $Sb(V)$ retention in natural minerals and soils, few considered the oxidation reaction of $Sb(III)$ in soils in the process of transport [14–17]. Earlier studies have studied the influence of dissolved molecular oxygen and hydrogen peroxide, iodate, natural minerals (Fe–Mn oxyhydroxides, etc.) on the oxidation of $Sb(III)$ to $Sb(V)$ [12,18–24]. These studies indicated that natural minerals with large surface areas not only can adsorb Sb strongly but also acting as oxidants in transforming $Sb(III)$ to $Sb(V)$. Photoirradiation of natural water samples spiked with $Sb(III)$ showed that the oxidation rates could be well predicted based on DOC [25]. Mitsunobu et al. [26] have studied Sb behavior under various redox conditions in soils, they found that $Sb(V)$ is a stable oxidation state even under reducing condition ($E_h = -180\ \text{mV}$, pH 8) and Sb is oxidized at lower E_h than arsenic. Interestingly, using $\mu\text{-XANES}$ method Mitsunobu et al. [27] proved that Sb reduction occurred in reducing soil which can be an important factor for Sb immobilization under reducing conditions, since the $Sb(III)$ sorbs more strongly on $Fe(III)$ hydroxides than $Sb(V)$ and its solubility is also much lower than that of $Sb(V)$ species. However, to our knowledge the redox chemistry of Sb in natural soil–water systems is still unclear. Furthermore, although Zhang et al. [28] have proven numerical models incorporating kinetic reactions and transport processes was capable of simulating $Sb(V)$ transport in soil columns, their capability in simulating the retention and transport of $Sb(III)$ in soils has not been evaluated.

In this study, kinetic batch and column transport experiments were carried out to (1) quantify the kinetics of oxidation and adsorption of $Sb(III)$ in two soils with contrasting properties; (2) evaluate the mobility of $Sb(III)$ in soils with miscible-displacement experiments; and (3) develop a reactive transport model to simulate the movement of $Sb(III)$ in soils for risk assessment of Sb exposure. Understanding the mechanism of $Sb(III)$ oxidation by soil is helpful in clarifying the fate and geochemical cycling of Sb in the environment. This study will provide essential information for eval-

uating the environmental risks associated with Sb transformation and mobilization at contaminated sites.

2. Material and methods

2.1. Soils and reagents

The studied samples of an acid red soil (Yingtian) and a calcareous soil (Huanjiang) were collected from Yingtian Red Soil Ecological Experiment Station and Huanjiang Observation and Research Station for Karst Ecosystems, respectively (for details, see the Supplementary Material). The chemicals used were of analytical grade or guaranteed grade (for details, see the Supplementary Material).

2.2. Batch experiments

Sorption isotherms on the two soils were determined using batch experiments at room temperature ($25\ ^\circ\text{C}$) under aerobic conditions [29]. The initial concentrations (C_0) of Sb_{tot} were 0.009, 0.047, 0.094, 0.472, and 0.944 mM. Experiments were initiated by mixing 3.0 g of soil with 30 mL of Sb solution in 50-mL Teflon tubes. The mixtures were shaken at 200 rpm on a reciprocal shaker for 48 h and subsequently centrifuged for 10 min at 4000 rpm before sampling.

To determine extent of time-dependent sorption and oxidation kinetic, batch experiments were initiated with three initial concentrations C_0 (0.09, 0.47, and 0.94 mM) of Sb_{tot} . The mixtures were sampled at reaction times of 0.5, 2, 6, 12, 24, 48, 168, and 240 h. Samples for $Sb(III)$ analysis were stabilized in 0.5 M disodium-hydrogen-citrate solution, and samples for Sb_{tot} ($Sb_{tot} = Sb(III) + Sb(V)$) determination were stabilized in 3 M HCl solution [19]. Amount of Sb_{tot} adsorption was calculated from the difference between concentrations of the supernatant and that of the initial solutions. For each input concentration C_0 , the tests were performed in triplicates and the mean and standard error (SE) of the amount of $Sb(III)$ and Sb_{tot} adsorbed is reported.

2.3. Miscible displacement experiments

The saturated miscible displacement technique was used to investigate the reactive transport of $Sb(III)$ in soils [30,31]. Two acrylic columns (8.5-cm in length and of 2.5-cm i.d.) were uniformly packed with Yingtian and Huanjiang soil samples. Soil bulk density of Yingtian soil was $1.36\ \text{g cm}^{-3}$ which is a little higher than Huanjiang soil of $1.19\ \text{g cm}^{-3}$. Pore volume of Yingtian and Huanjiang soils in the columns were 21 and 24 mL respectively. Two columns were slowly water saturated with background solution at a low Darcy flux until effluent pH reached steady state, about 4.0 for red soil and 7.9 for calcareous soil. Input solution of 0.094 mM Sb_{tot} was subsequently introduced to each soil column at constant flow rate (about $7\ \text{mL h}^{-1}$) with a peristaltic pump (BT 102S, Baoding Longer Precision Pump Co., Ltd., Hebei, China). The Sb solution was continuous purging of nitrogen gas throughout the whole process of experiment and the purity of nitrogen gas was 99.95%. A leaching or desorption pulse consists of pumping the background solution was conducted after applying Sb solution. Effluent samples were collected from the outlet of the column by an automatic effluent fraction collector (CBS-A, Shanghai Huxi Analysis Instrument Factory Co., Ltd., Shanghai) at 1 h time interval.

Concentrations of $Sb(III)$ and Sb_{tot} were analyzed using Hydride Generation Atomic Fluorescence Spectrometer (AFS-930, Beijing Jitian Instrument Factory Co., Ltd., Beijing) [19], and the concentration of $Sb(V)$ was calculated from the difference of Sb_{tot} and $Sb(III)$ concentrations. The pH of the solutions (0.1 units) was measured using a pH meter (Metrohm 713) and a combined glass electrode

(Metrohm 6.0222.100), which was calibrated with buffer solutions (Merck).

2.4. Modeling

The interactions of Sb(III) and Sb(V) with the soils were modeled using the computer program PHREEQC [32]. The model assumes that Sb(V)/Sb(III) is retained on soil at a set of equilibrium sorption sites interacts instantaneously and a set of reversible kinetic sites are time dependent in nature. The oxidation of Sb(III) to Sb(V) occur only on soil surface and the oxidation kinetics is linearly related to adsorbed Sb(III) (Fig. 1). The model can be described in the following formulations:

$$S_{Sb(III)eq} = K_{d3}C_{Sb(III)} \quad (1)$$

$$\frac{\partial S_{Sb(III)k}}{\partial t} = k_{f3}C_{Sb(III)} - k_{b3}S_{Sb(III)k} \quad (2)$$

$$S_{Sb(V)eq} = K_{d5}C_{Sb(V)} \quad (3)$$

$$\frac{\partial S_{Sb(V)k}}{\partial t} = k_{f5}C_{Sb(V)} - k_{b5}S_{Sb(V)k} \quad (4)$$

$$\frac{\partial C_{Sb(V)}}{\partial t} = k_{ox}S_{Sb(III)} \quad (5)$$

Here $S_{Sb(III)eq}$ and $S_{Sb(V)eq}$ are the Sb(III) or Sb(V) retained on equilibrium sites ($\mu\text{mol g}^{-1}$), $S_{Sb(III)k}$ and $S_{Sb(V)k}$ are the Sb(III) or Sb(V) retained on kinetic type sites ($\mu\text{mol g}^{-1}$), $S_{Sb(III)}$ is the sum of $S_{Sb(III)eq}$ and $S_{Sb(III)k}$ that is all Sb(III) retained on soil surface ($\mu\text{mol g}^{-1}$), $C_{Sb(III)}$ and $C_{Sb(V)}$ are the Sb(III) and Sb(V) concentration in solution ($\mu\text{mol L}^{-1}$), K_{d3} and K_{d5} are the equilibrium distribution coefficient, k_{f3} , k_{f5} and k_{b3} , k_{b5} (h^{-1}) are the forward and backward reaction rates associated with kinetic sites, respectively, k_{ox} is the oxidation rate of Sb(III) on soil surface, t is reaction time. To simulate the reactive transport of Sb(III) and Sb(V) through soils, the kinetic reaction formulations are incorporated into the steady state convection–dispersion equation (CDE) in the form of:

$$\frac{\partial C_{Sb(III)}}{\partial t} + \frac{\partial S_{Sb(III)}}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C_{Sb(III)}}{\partial x} \right) - v \frac{\partial C_{Sb(III)}}{\partial x} \quad (6)$$

$$\frac{\partial C_{Sb(V)}}{\partial t} + \frac{\partial S_{Sb(V)}}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C_{Sb(V)}}{\partial x} \right) - v \frac{\partial C_{Sb(V)}}{\partial x} \quad (7)$$

where x is distance (cm), D is hydrodynamic dispersion coefficient ($\text{cm}^2 \text{h}^{-1}$), and v is pore water velocity (cm h^{-1}).

3. Results and discussion

3.1. Sorption isotherms

Langmuir and Freundlich models were used to fit our experimental adsorption data for describing the distribution of $S_{b_{tot}}$ between aqueous (C) and two soils (S), the corresponding sorption parameters were derived by plotting the linear forms of both isotherms. The results are shown in Fig. 2 and Table 1. The Freundlich equation can be expressed as $S = K_F C^N$, where S represents the amount of adsorption ($\mu\text{mol g}^{-1}$), K_F is the Freundlich distribution or partition coefficient (L g^{-1}), C is equilibrium concentration

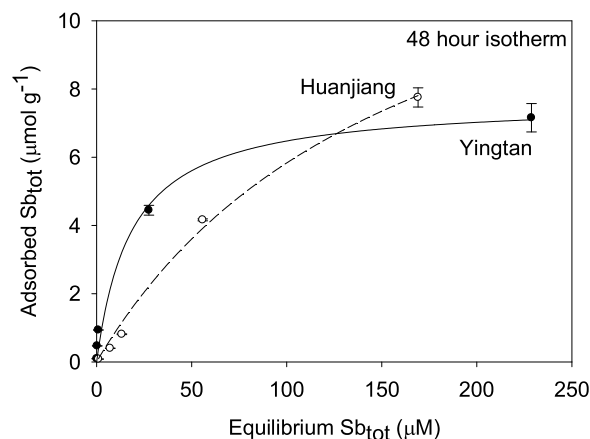


Fig. 2. Sorption isotherms of $S_{b_{tot}}$. The solid and dashed lines depict results of curve-fitting with the Langmuir model. The experiments were performed by 48 h reaction of 3 g soil with 30 mL Sb solutions at different initial concentrations.

($\mu\text{mol L}^{-1}$), and N is the dimensionless reaction order. The Langmuir equation is another widely use equilibrium sorption model which has the advantage of providing a sorption maximum S_{max} ($\mu\text{mol g}^{-1}$) that can be correlated to sorbed phases sorption properties. The Langmuir equation has the form $S = S_{max} \frac{K_L C}{1 + K_L C}$, where K_L ($\text{L } \mu\text{mol}^{-1}$) is a Langmuir coefficient related to the binding strength, C is equilibrium concentration ($\mu\text{mol L}^{-1}$). The Langmuir isotherm model assumes that all adsorption sites have equal affinity for the adsorbate and therefore only monolayer adsorption occurs while the Freundlich isotherm is based on the assumption of heterogeneous surfaces with different affinities that is have multilayer adsorption [33].

Fig. 2 clearly exhibit the nonlinear adsorption behavior of Sb, which is characterized by the low values of the Freundlich non-linear reaction order for Yingtan ($N = 0.32 \pm 0.05$) and Huanjiang ($N = 0.73 \pm 0.10$) soil. The two models were well fitted the adsorption of $S_{b_{tot}}$ on the two soils which have high regression coefficients (>0.975) for all cases (Table 1). A comparison between the Langmuir parameters demonstrated that the maximum adsorption of $S_{b_{tot}}$ on Huanjiang soil ($15.30 \pm 2.40 \mu\text{mol g}^{-1}$) was about two times of the Yingtan soil ($7.67 \pm 0.56 \mu\text{mol g}^{-1}$). Several studies have found that soil properties including metal content, organic matter as potential controlling factors of Sb retention and transport in soils [17,34,35]. This is consistent with the soil characteristics that there are more TOC and iron and manganese oxides in the Huanjiang soil than the Yingtan soil. While the adsorption amount of $S_{b_{tot}}$ on Huanjiang soil was a little lower than Yingtan soil at the lower initial concentrations, and at the highest initial concentration the adsorption amount on Huanjiang soil was much higher (Fig. 2). The adsorption isotherms of $S_{b_{tot}}$ in Fig. 2 was different from Sb(V) adsorption results from our previous study [28], which showed that the adsorption of Sb(V) in Yingtan soil was much higher than in Huanjiang soil. This is because that Sb(V) adsorption was dramatically influenced by solution pH while Sb(III) can be adsorbed in a wide range of pH [35].

Sb(III) and Sb(V) concentrations in the equilibrium solution after sorption isotherms experiment are shown in Fig. 3 illustrate that

Table 1
Estimated Freundlich- and Langmuir- parameters for $S_{b_{tot}}$ adsorption.

Sb	Soil	Langmuir			Freundlich		
		$S_{max} \mu\text{mol g}^{-1}$	$K_L \mu\text{mol}^{-1}$	R^2	$K_F \text{ L g}^{-1}$	N	R^2
$S_{b_{tot}}$	Yingtian	7.67 ± 0.56	0.054	0.987	1.27 ± 0.32	0.32 ± 0.05	0.975
	Huanjiang	15.30 ± 2.40	0.006	0.994	0.189 ± 0.09	0.73 ± 0.10	0.982

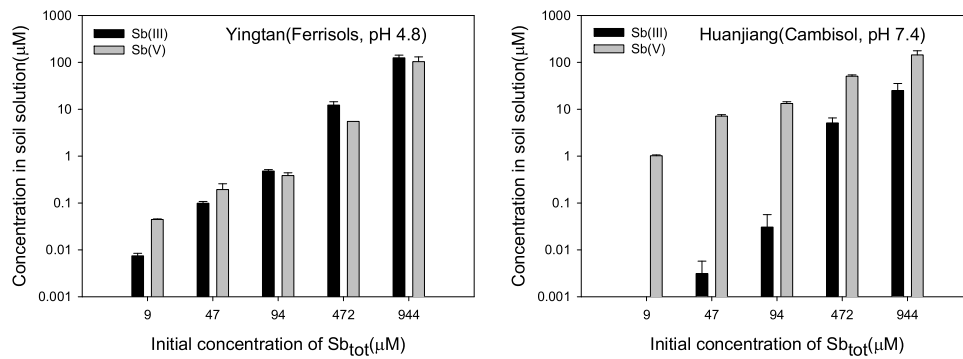


Fig. 3. Sb(III) and Sb(V) concentration in equilibrium soil solution of Yingtan (left plot) and Huanjiang (right plot) soil at five initial concentrations (0.009, 0.047, 0.094, 0.472, and 0.944 mM), the black and gray bars depict Sb(III) and Sb(V) concentrations in soil solutions, respectively.

abundant of Sb(V) existed especially in the Huanjiang soil solution. At the three lower initial concentrations, almost all Sb sorbed in Yingtan soil with little Sb(V) released but there was more Sb(V) released in Huanjiang soil. At the two higher initial concentrations, about 50% of Sb_{tot} was Sb(III) in the Yingtan soil solutions, and in the Huanjiang soil solutions Sb(III) was less than 20% of Sb_{tot} . The difference between the two soils may be because of the physical and chemical characteristics, especially the TOC and Fe-Mn oxides contents and the pH in the solution. As earlier studies have indicated that content of TOC and Fe-Mn oxides dramatically influence adsorption of Sb, and pH can influence the oxidation rate of Sb(III) and release of Sb(V) from soil [12,36,37]. Belzile et al. [24] have studied on the oxidation of Sb(III) in presence of natural and synthetic iron and manganese oxyhydroxides, indicated that Sb(III) can rapidly be oxidized to Sb(V) by them. So the existence of soils we studied here might be one reason of Sb(III) oxidization, as the two soils have high content of Fe-Mn oxides especially in Huanjiang soil.

3.2. Kinetic oxidation and sorption

The results of control experiment where no soil was added clearly demonstrated that concentration of Sb(III) did not change for 240 h throughout the experiment (for details, see the Supplementary Material). This may be because the compounds (potassium antimony tartrate) that we used to prepare Sb(III) solution is very stable in aqueous solutions. Calle-Gutiérrez et al. [46] had found that Sb(III) in aqueous solutions stored at room temperature of 25 °C was not oxidized to Sb(V) after 3 months using the same compound. Furthermore, The result was also consistent with the study of Belzile et al. [24], where no significant oxidation of Sb(III) was observed in solution with O_2 but without Fe-Mn oxides in the pH range of 5–10 within 7 days.

The results of kinetic batch experiments are presented in Fig. 4 and Fig. 5. The time series of Sb(III) and Sb(V) concentration in Fig. 4 clearly illustrates the oxidation of Sb(III) and release of Sb(V) on/from soil surface. Concentration of Sb(III) in soil solution continuously decreased during the kinetic experiment, while concentration of Sb(V) in soil solution increased firstly and then decreased. The initial dramatic decrease of Sb(III) indicated a strong adsorption process. The phenomenon that Sb(V) increased firstly and then decreased is similar to the results of As(III) oxidation on aquifer material surfaces [47]. This suggest a multi-step surface adsorption-oxidation process: (1) transport of Sb(III) to the surface, (2) Sb(III) adsorption onto the surface sites, (3) oxidation of Sb(III) to Sb(V) at the surface, (4) release of produced Sb(V) from the surface, and (5) Sb(V) adsorption to other surface sites following its production and release into solution.

Comparison between the two soils revealed that a larger fraction of Sb(III) was transformed into Sb(V) in Huanjiang soil than in

Yingtan soil, which is consistent with the result of isotherm adsorption experiment. Our experiments indicated that oxidation of Sb(III) was slower in Yingtan soil than in Huanjiang soil. The higher pH of the Huanjiang soil (>7.0) could be one major factor controlling the release of Sb(V). In addition, the difference in the soil content of manganese oxides might also be a contributing factor to the oxidation capacity of the two soils.

The changes of Sb_{tot} adsorption with reaction time shown in Fig. 5 demonstrated that the oxidation-sorption process of Sb(III) in soils. The rate of Sb_{tot} retention was rapid during the earlier stages of reaction and then followed by slow reactions. This is consistent with previous studies which revealed that Sb adsorption was initially rapid followed by a slow retention rate [12,19]. The retention rate of Sb was rapid at low initial concentrations especially in Yingtan soil solution, which indicated that preferential sorption of Sb on high energy sites. But in the slow reaction of Sb adsorption process the adsorption amount of Sb_{tot} have a little decrease especially in the Huanjiang soil. This is because of Sb(III) was oxidized to Sb(V) on soil surface and then released, and as the extension of the experimental time, Sb(V) was readsorbed on the soils again. Tighe and Lockwood [38] have reported that 95% Sb(V) sorption by a non-crystalline Fe hydroxide across a pH range of 2.5–7 with a sorption maximum at about pH 4. Sorption of Sb(V) on hematite is also strong, with a similar sorption maxima (~pH 4) involving a combination of surface binding sites, similar to arsenic [39,40]. At the time of 48 h, the kinetic adsorption amount were 0.91 ± 0.01 , 4.12 ± 0.03 , $6.10 \pm 0.04 \mu\text{mol g}^{-1}$ for three initial concentrations of Sb in the Yingtan soil. While the isotherm adsorption amount were 0.94 ± 0.01 , 4.45 ± 0.20 , $7.16 \pm 0.59 \mu\text{mol g}^{-1}$ (Fig. 2) for the same three initial concentrations. The reason of the difference is that in the kinetic experiment more oxygen could involve in the redox process, and this cause more Sb(III) oxidized and released from soil surface. The phenomenon appeared more significantly in Huanjiang soil, in the kinetic experiment the amount of Sb_{tot} was 0.76 ± 0.01 , 3.29 ± 0.03 , $5.90 \pm 0.06 \mu\text{mol g}^{-1}$, which is much less than 0.81 ± 0.01 , 4.16 ± 0.03 , $7.75 \pm 0.28 \mu\text{mol g}^{-1}$ (Fig. 2) of the isotherm adsorption experiment.

Our model successfully simulated the oxidation and sorption process of Sb(III) in the two soils. The modeling results clearly shows that the equilibrium distribution coefficient K_{d3} and K_{d5} were higher in Yingtan soil than in Huanjiang soil in the batch experiments at all the three initial concentrations (Table 2). And the higher of the initial concentration, the lower of the equilibrium distribution coefficient. But in the column experiments, the equilibrium distribution coefficient K_{d3} and K_{d5} were higher in Huanjiang soil than in Yingtan soil. The sorption reaction rate of Sb(III) was higher in Huanjiang soil than in Yingtan soil which is contrary to Sb(V). While the oxidation reaction rate was lower in Yingtan soil than in Huanjiang soil for all of the experiments. In Yingtan soil,

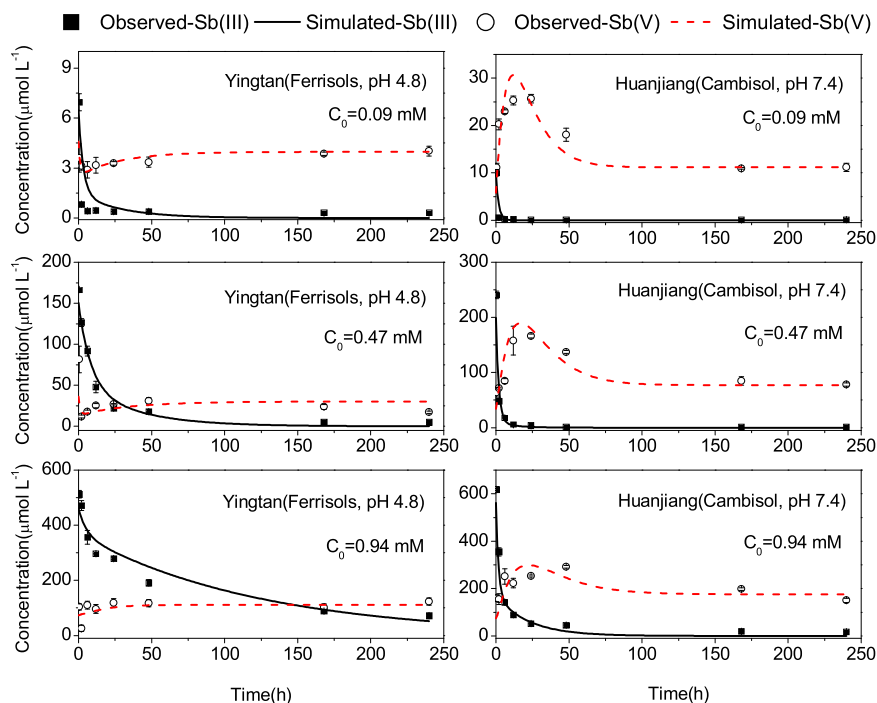


Fig. 4. Concentrations of Sb(III) and Sb(V) in Yingtan and Huanjiang soil solutions for the whole process of kinetic batch experiments with three initial concentrations (0.09, 0.47, and 0.94 mM). The left three plots depict Yingtan soil solution, and right three plots depict Huanjiang soil solution. The black squares and white circles are the measured concentrations of Sb(III) and Sb(V), respectively. The solid and dash lines are model fits to the experimental data.

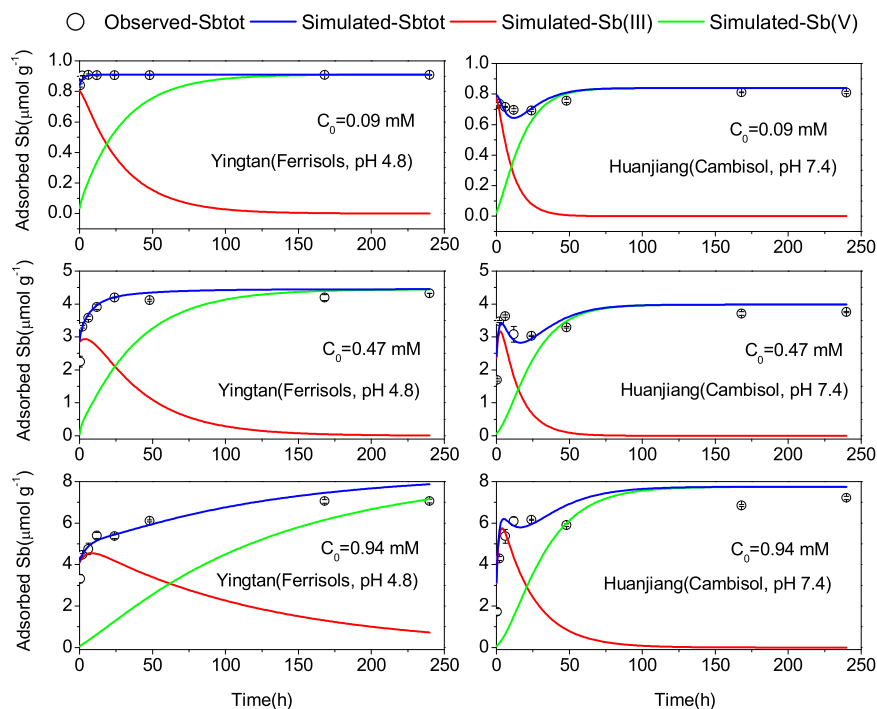


Fig. 5. Sorption kinetics of Sb on two soils at three initial concentrations (0.09, 0.47 and 0.94 mM) of Sb_{tot} . The experiments were performed by mixing 3 g soil with 30 mL Sb solution prepared in 0.01 M KCl. The left three plots depict Yingtan soil solution, and the right three plots depict Huanjiang soil solution. Symbols are for the measured Sb_{tot} adsorbed on soils. The red, green, and blue lines indicate Sb(III), Sb(V), and Sb_{tot} adsorbed on soils by model simulation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the oxidation rate clearly influenced by the initial concentration of Sb(III). After 240 h reaction, almost all Sb(III) adsorbed on soils were oxidized to Sb(V) for the two lower initial concentrations (0.09, 0.47 mM), but it need more time for all Sb(III) to be oxidized when the initial concentration was 0.94 mM (Fig. 4). At the three con-

centrations 0.09, 0.47, and 0.94 mM the oxidation rates of Sb(III) were $9.72E-06$, $8.33E-06$, and $3.89E-06$ (Table 2). In Huanjiang soil, almost all Sb(III) was oxidized in about 150 h because of relatively higher oxidation rate. Overall, Sb(III) will be oxidized to Sb(V) fast after adsorbed onto the two soil surfaces and Sb(V) can be eas-

Table 2

Comparison of sorption and oxidation parameters (K_d , k_f , k_b and k_{ox}) from fitting kinetic model to kinetic batch data and column transport at different initial concentration (C_0).

Experiment	Soil	C_0 (μM)	K_{d3}	k_{f3} (s^{-1})	k_{b3} (s^{-1})	k_{ox} (s^{-1})	K_{d5}	k_{f5} (s^{-1})	k_{b5} (s^{-1})
Batch	Yingtang	0.09	31.6	8.33E-04	2.78E-05	9.72E-06	10.0	3.39E-04	1.53E-05
		0.47	5.0	5.56E-05	1.67E-05	8.33E-06	1.6	2.22E-04	1.53E-05
		0.94	2.5	1.94E-05	4.17E-05	3.89E-06	1.6	1.67E-05	2.22E-06
	Huanjiang	0.09	20.0	1.11E-03	2.78E-05	2.78E-05	5.0	2.78E-05	3.89E-06
		0.47	3.2	2.78E-04	2.78E-05	2.22E-05	2.5	1.67E-05	3.33E-06
		0.94	1.6	1.67E-04	5.56E-05	1.53E-05	1.6	1.81E-05	4.17E-06
Column	Yingtang	0.94	100.0	8.33E-05	2.78E-08	1.39E-08	100.0	2.22E-04	1.39E-05
	Huanjiang	0.94	316.2	8.89E-05	4.17E-08	3.33E-08	794.3	9.72E-05	2.78E-06

ily released into solution and then readsorbed in Huangjiang soil (Figs. 4 and 5).

3.3. Breakthrough curves

Fig. 6 shows the breakthrough curves of Sb(III) and Sb(V) in columns of the two soils. Extensive retention and low mobility of Sb(III) was found in the two soils before 100 pore volumes of Yingtang soil and 150 pore volumes of Huanjiang soil. This result was different with the result of Sb(V) study by Zhang et al. [28] in the same two soils. In their study Sb(V) can easily breakthrough the soil column of Huanjiang soil, while for Yingtang soil Sb(V) was extensive retention. Complete breakthrough, i.e. 100% recovery of that input concentration of Sb, was observed in the Yingtang soil column after applying 180 pore volumes of Sb(III) solution. While for the Huanjiang soil column, Sb was far from complete breakthrough. In Yingtang soil column, almost no Sb effluent before the first 90 pore volumes. But after 90 pore volumes, the Sb breakthrough the column quickly, and the vast majority of Sb was Sb(III). This may be because of red colloid formed in the soil column after applying 100 pore volumes of Sb(III) solution. And the main colloid Sb was Sb(III) and the colloid mainly composed of Fe-oxides (Fe weight percentage 8.69%) which was analyzed by SEM-EDS. Earlier studies have indicated that colloid is an important factor influence heavy metals transport in soils [41,42]. Huanjiang soil has a larger adsorption capacity than Yingtang soil, which is consistent with the result of isotherms experiment (Table 1). The peak Sb_{tot} concentration in the effluent of Huanjiang soil column was only about 15% of the applied concentration after applying approximately 300 pore volumes of Sb solution. This is contrary to the transport behavior of Sb(V) in the same two soils [28]. It means that Sb(III) has strong mobility in acidic Yingtang soil with colloid of Fe-oxides, while on the contrary Sb(V) was more easily transport in calcareous Huanjiang soil. When leaching with KCl solution, almost no Sb(V) released from Yingtang soil column (Fig. 6), which is consistent with our kinetic experiment. This means that sorption of Sb(III) was irreversible especially in an anaerobic system, which was consistent with earlier studies [12,19,35,43].

In Huanjiang soil column, the concentration of Sb(V) in the effluent solution was far below the input solution before the first 150 pore volumes. After that Sb(III) and Sb(V) concentration in effluent began to increase slowly till to replace the input solution by KCl solution. The concentration of Sb(V) was continuing increase until applying about 200 pore volumes of KCl solution. After 200 pore volumes of KCl input, most of the Sb leached out was Sb(V). In calcareous Huanjiang soil Sb(V) showed a non-equilibrium transport process as the extensive tailing and slow release during leaching [28]. In our experiment the extensive tailing and slow release of Sb(V) was more significantly due to the oxidation rate of Sb(III) and abundant of Sb(III) adsorbed before leaching. Ilgen et al. [44] have found that in berm soils with high organic matter content, Sb(III) will have a longer half-life compared to soils with low organic content. So Sb(III) sorbed on Huanjiang soil with high content of TOC

might cause a long-term release of Sb(V). Mitsunobu et al. [26] have found that Sb was present exclusively as Sb(V) over a wide redox range (from Eh = 360 to -140 mV, pH 8) in the soil-water system. This means even in anaerobic conditions, Sb(III) might be oxidized to Sb(V) if there are oxidant such as Fe-Mn oxides exist in the system. Furthermore, we think it is unlikely that Sb(III) was oxidized by microbial processes in our system, as earlier studies have shown that a few bacteria able to oxidize antimony have been isolated from the environment [45] let alone in this anoxic conditions. Notably, in our experiment the two soils with widely natural minerals all have large surface areas, not only as adsorbent but also acting as strong oxidants in transforming Sb(III) to Sb(V). Overall, Sb(III) can easily breakthrough the vadose zone in anaerobic condition in acid Yingtang soils and may contaminate ground water, while Sb(III) sorbed on the calcareous Huanjiang soil might cause long-term release of Sb(V).

The model cannot well simulated Sb(III) and Sb(V) transport because of abundant of colloid carried Sb in the Yingtang soil column. While the model can well simulated Sb(III) and Sb(V) transport in Huanjiang soil column but overestimated the oxidation rate of Sb(III). Sorption rate coefficients (K_d) obtained from column BTCs are great larger than those from kinetic sorption data (Table 2), which is indicative of stronger equilibrium sorption in columns than in batch reactors. Compared with kinetic experiment, the oxidation rate coefficients (k_{ox}) is higher in batch reactors than in columns because the column experiment was conducted in anaerobic conditions. Other factors such as low soil/solution ratio and increased spatial heterogeneity of sorption sites might also contribute to the observed discrepancy between reaction systems [30].

4. Conclusions

Understanding the mechanisms controlling the kinetic retention, transport and redox process of Sb(III) is prerequisite for evaluating the environmental risk of Sb contaminated soils. In this study, the kinetic batch and column experiment results clearly revealed that a majority of input Sb(III) was kinetically oxidized into Sb(V) on surface of soils in kinetic batch experiment under aerobic condition and a smaller amount of Sb(III) was oxidized into Sb(V) in saturated column experiment under anaerobic condition. Sb(III) can easily breakthrough the vadose zone in anoxic condition in acid Yingtang soils and may contaminate ground water, this should be concern as Sb(III) is more toxicity than Sb(V). While the Sb(III) sorbed on the calcareous Huanjiang soil should also be considered as the long-term release of Sb(V) will cause continuous pollution. Soil is the catalyst and oxidant promoted the oxidation of Sb(III) even under anoxic conditions especially in calcareous soils. The equilibrium-kinetic sorption and kinetic oxidation formulations were capable of describing the kinetics of Sb(III) reactions. But the reactive transport model was less successful in describing the transport of Sb in soil columns especially in Yingtang soil column as abundant of colloid carried Sb leaching from the column and our model did not consider colloid species. Additional reaction mecha-

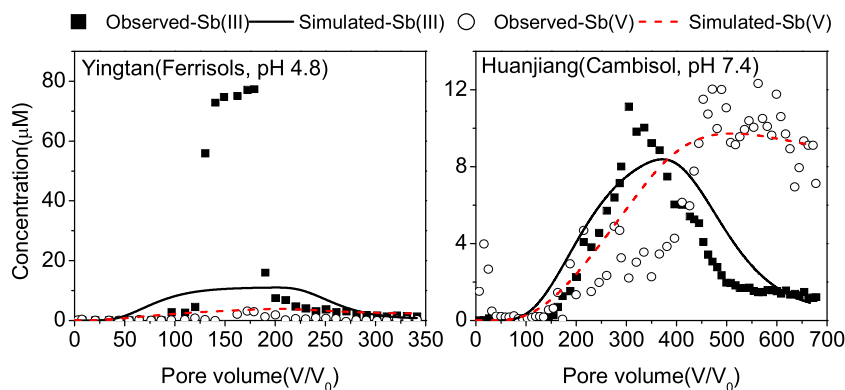


Fig. 6. Breakthrough curves of Sb(III) and Sb(V) from two soil columns. The left plot shows results of Yingtan soil column, and the right plot shows results of Huanjiang soil column. The black squares and white circles are the measured concentrations of Sb(III) and Sb(V) in effluent of columns. The solid and dash lines are model fits to the experimental data of Sb(III) and Sb(V), respectively.

nisms including colloid facilitated transport may contribute to the mobility of Sb(III) in soils.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.05.027>.

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